Inorg. Chem. **1998,** *37,* 153−155

Homo- (4f, 4f) and Heterodimetallic (4f, 4f′) Complexes. The First Structurally Characterized Example of a Heterodimetallic (Yb, La) Complex (1′). Magnetic Properties of 1′ and of a Homodinuclear (Gd, Gd) Analogue

J.-P. Costes,* F. Dahan, A. Dupuis, S. Lagrave, and J.-P. Laurent

Laboratoire de Chimie de Coordination du CNRS,
UPR 8241 liée par convention à l'Université Paul Sabatier,
205 route de Narbonne, 31077 Toulouse Cedex, France

Received October 1, 1997

In recent years, an increasing interest has been given to the magnetic properties of dinuclear[1] complexes comprising simultaneously either 4f and 3d ions or identical 4f ions.[2−8] However, we are not aware of any example of a structurally characterized complex involving two different lanthanide (4f, 4f′) ions. In an attempt to obviate the dearth of experimental data, we have reconsidered the coordination properties of tripodal ligands. Indeed, ligands of this type have been employed as hosts for 3d or 4f ions, leading to mononuclear (3d or 4f) and homodinuclear (4f, 4f) complexes.[9−18] Very recently, it was shown that a mononuclear (4f) complex prepared from a novel tripodal ligand can be deprotonated to incorporate a Ni^{2+} ion.[19] Also, relevant to the present paper is the use of 3d-block tripods in obtaining self-assembled triple-stranded heterodinuclear (3d, 4f) complexes.[20]

The aim of the present contribution is to demonstrate the effectiveness of a potentially decadentate Schiff base LH_3[21] (tris-[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]amine) in generating hetero- (4f, 4f′) as well as homodimetallic (4f, 4f) species. A schematic representation of LH_3 is given in Figure 1. Three complexes will be considered to exemplify both possibilities. Crystals suitable for an X-ray diffraction study have been obtained for a complex involving the (Yb, La) couple. To our knowledge, this is the first structurally characterized example of a heterodimetallic lanthanide complex.

Experimental Section

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]amine. This ligand was obtained as previously described.[21]

[Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]aminato-(3−)]ytterbium(III) Hemihydrate. To a mixture of LH_3 (0.27 g, 5×10^{-4} mol) and $CsOH{\cdot}H_2O$ (0.50 g, 1.5×10^{-3} mol) in methanol (20 mL) was added $Yb(NO_3)_3{\cdot}5H_2O$ (0.22 g, 5×10^{-4} mol). After a gentle heating (20 min), the yellow precipitate that appeared was filtered off after cooling and washed with water, cold methanol, and diethyl ether. Yield: 0.33 g (90%). Anal. Calcd for $C_{30}H_{34}N_4O_{6.5}Yb$: C, 49.5; H, 4.7; N, 7.7. Found: C, 49.3; H, 4.3; N, 7.7. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 720$ (100), $[LYb + 1]^+$.

[Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]aminato-(3−)]gadolinium(III)cesium Nitrate Trihydrate. Using the same procedure and $Gd(NO_3)_3{\cdot}5H_2O$, we could not isolate the neutral complex LGd, but only the $LGdCs(NO_3){\cdot}3H_2O$ entity. Yield: 65%. Anal. Calcd for $C_{30}H_{39}CsGdN_5O_{12}$: C, 37.9; H, 4.1; N, 7.4. Found: C, 37.4; H, 3.7; N, 7.4. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 836$ (100), $[LGdCs]^+$.

[Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]aminato-(3-)]ytterbium(III)lanthanum(III) Nitrate Dihydrate (1). A mixture of $LYb{\cdot}0.5H_2O$ (0.36 g, 5×10^{-4} mol) and $La(NO_3)_3{\cdot}6H_2O$ (0.22 g, 5×10^{-4} mol) in methanol (20 mL) was stirred until a light yellow precipitate appeared. The precipitate was filtered off and washed with methanol and diethyl ether. Yield: 0.32 g (60%). Anal. Calcd for $C_{30}H_{37}LaN_7O_{17}Yb$: C, 33.4; H, 3.4; N, 9.1. Found: C, 33.1; H, 3.1; N, 8.9. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 982$ (100), $[LYbLa(NO_3)_2]^+$.

Slow diffusion of diethyl ether into a filtered acetone solution of $LYb{\cdot}0.5H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ in excess yielded crystals suitable for X-ray diffraction study. They analyzed as $L_2Yb_2(C_3H_6O)_2La_3(NO_3)_9{\cdot}H_2O$ (**1′**). Anal. Calcd for $C_{66}H_{80}La_3N_{17}O_{42}Yb_2$: C, 31.1; H, 3.1; N, 9.3. Found: C, 30.4; H, 2.7; N, 9.1. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 982$ (100), $[LYbLa(NO_3)_2]^+$. Mass spectrum (FAB$^-$, 3-nitrobenzyl alcohol matrix): $m/z = 387$ (58), $[La(NO_3)_4]^-$.

[Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]aminato-(3−)]digadolinium(III) Nitrate Trihydrate (2). Starting with $LGdCs(NO_3){\cdot}3H_2O$ and $Gd(NO_3)_3{\cdot}5H_2O$ and using the same procedure as above yielded the digadolinium complex. Yield: 63%. Anal. Calcd for $C_{30}H_{39}Gd_2N_7O_{18}$: C, 32.7; H, 3.5; N, 8.9. Found: C, 32.6; H, 3.1; N, 8.5. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 985$ (100), $[LGd_2(NO_3)_2]^+$.

Materials and Methods. All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N) were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse, France. Magnetic susceptibility data were collected on a powdered sample of the

---

[1] The analysis of magnetic data is greatly facilitated by considering insulated dinuclear complexes. Cf. refs 2 and 3.

[2] Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *Inorg. Chem.* **1996**, *35*, 2400 and references therein.

[3] Ramade, I.; Kahn, O.; Jeannin, Y.; Robert, F. *Inorg. Chem.* **1997**, *36*, 930 and references therein.

[4] Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *Inorg. Chem.* **1997**, *36*, 3429; see also references therein.

[5] Wang, S.; Pang, Z.; Smith, K. D. L.; Hua, Y.; Delippe, C.; Wagner, M. J. *Inorg. Chem.* **1995**, *34*, 908 and references therein.

[6] Panagiotopoulos, A.; Zafiropoulos, T. F.; Perlepes, S. P.; Bakalbassis, E.; Masson-Ramade, I.; Kahn, O.; Terzis, A.; Raptopoulou, C. P *Inorg. Chem.* **1995**, *34*, 4918 and references therein.

[7] Kahwa, I. A.; Folkes, S.; Williams, D. J.; Ley, S. V.; O'Mahoney, C. A.; McPherson, G. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1531 and references therein.

[8] Costes, J. P.; Dupuis, A.; Laurent, J. P. *Inorg. Chim. Acta*, in press; see also references therein.

[9] Smith, A.; Rettig, S. J.; Orvig, J. C. *Inorg. Chem.* **1988**, *27*, 3929.

[10] Berg, D. J.; Rettig, S. J.; Orvig, C. *J. Am. Chem. Soc.* **1991**, *113*, 2528.

[11] Yang, L.; Liu, S.; Wong, E.; Rettig, S. J.; Orvig, J. C. *Inorg. Chem.* **1995**, *34*, 2164.

[12] Blech, P.; Floriani, C.; Chiesti-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 3557.

[13] Jones, P. L.; Amoroso, A. J.; Jeffery, J. C.; McCleverty, J. A.; Psillakis, E.; Rees, L. H.; Ward, M. D. *Inorg. Chem.* **1997**, *36*, 10.

[14] Kocian, O.; Chiu, K. W.; Demeure, R.; Gallez, B.; Jones, C. J.; Thornback, J. R. *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 527.

[15] Cook, D. F.; Cummins, D.; McKenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1976**, 1369.

[16] Liu, S.; Gelmini, L.; Rettig, S. J.; Thompson, R. C.; Orvig, C. *J. Am. Chem. Soc.* **1992**, *114*, 6081.

[17] Yang, L.; Liu, S.; Rettig, S. J.; Orvig, J. C. *Inorg. Chem.* **1995**, *34*, 4921.

[18] Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163.

[19] Archibald, S. J.; Blake, A. J.; Parsons, S.; Schröder, M.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1997**, 173.

[20] Piguet, C.; Rivara-Minten, E.; Bernardinelli, G.; Bünzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 421.

[21] Liu, S.; Yang, L. W.; Rettig, S. J.; Thompson, R. C.; Orvig, C. *Inorg. Chem.* **1993**, *32*, 2773.

S0020-1669(97)01248-2 CCC: $15.00

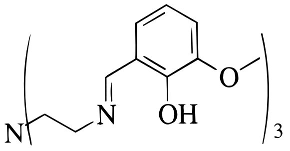

Figure 1. Schematic representation of the LH_3 ligand.

Table 1. Crystallographic Data for $\{[LYb(C_3H_6O)La(NO_3)_2]_2La(NO_3)_5(H_2O)\}$ (**1′**)

empirical formula	$C_{66}H_{80}La_3N_{17}O_{42}Yb_2$	fw	2546.28
a	24.717(2) Å	*T*	293(2) K
b	16.159(2) Å	λ	0.710 73 Å
c	24.530(2) Å	D_{calc}	1.726 g cm^{-3}
β	96.032(9)°	μ_{calc}	32.62 cm^{-1}
V	9797(2) Å^3	R^a: all obsd	0.0678, 0.0454
Z	4	$R_w{}^b$: all obsd	0.0985, 0.0726

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w(|F_o{}^2|)^2]^{1/2}$.

compound with use of a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants[22] (-442×10^{-6} emu mol^{-1}). Positive and negative FAB mass spectra were recorded in dmf as a solvent and 3-nitrobenzyl alcohol matrix with a Nermag R10-10 spectrometer. Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Crystal data are gathered in Table 1.

Results and Discussion

The synthesis of LH_3 was reported earlier,[21] but to our knowledge, its coordination chemistry has not been studied. Indeed, successive reactions of the trideprotonated form of the ligand LH_3 in methanol with two appropriate lanthanide nitrates first yielded the related mononuclear species LLn (Ln = Yb, Gd) and then the dinuclear species $LYbLa(NO_3)_3$ (**1**) and $LGd_2(NO_3)_3$ (**2**). In both cases, we failed to obtain crystals suitable for an X-ray diffraction study, but the nature of **1** and **2** was firmly identified by elemental analysis and spectroscopic data. The FAB$^+$ mass spectra of **1** and **2** exhibit an intense peak (*m/z* = 982 for **1** and 985 for **2**) corresponding to $[LLnLn'(NO_3)_2]^+$. The presence of two, different or identical, lanthanide ions is further supported by the isotopic patterns. Surprisingly, well-shaped crystals were obtained in one case where the mononuclear precursor LYb was reacted with a 2-fold excess of $La(NO_3)_3 \cdot 5H_2O$ in acetone. They analyzed as $L_2Yb_2(C_3H_6O)_2La_3(NO_3)_9 \cdot H_2O$ (**1′**). A possible structure was suggested by mass spectra (FAB$^+$ and FAB$^-$) and charge balance considerations. So, in the case of **1′**, the main peak of the FAB$^+$ spectrum appears at *m/z* = 982 and may be attributed to $[LYbLa(NO_3)_2]^+$, while, in the FAB$^-$ spectrum, a signal at *m/z* = 387 has to be related to the anion $[La(NO_3)_4]^-$. The corresponding peak is not present in the FAB$^-$ spectrum of **1**. Complex **1′** would involve two $[LYbLa(NO_3)_2]^+$ monocationic units and one $[La(NO_3)_5(H_2O)]^{2-}$ dianionic unit.

Complexes **1**, **2**, and **1′** give rise to very similar infrared spectra in the 400−4000 cm^{-1} range. The bands attributable to the deprotonated ligand (ν_{CC}, ν_{CN}, ν_{CO}) occur at the same positions (1618(±5), 1449(±5), and 1221(±3) cm^{-1}). In the three cases, there is no absorption characteristic of ionic nitrates but bands attributable to bidentate nitrates are observed at 1463(±5) and 1325(±5) cm^{-1}. These spectral data support the view that, apart from the number of coordinated nitrates and, consequently, the nature of these species, neutral or ionic, the structures of **1** and **2** may exhibit great similarities to that of the cationic unit of **1′** (*vide infra*).

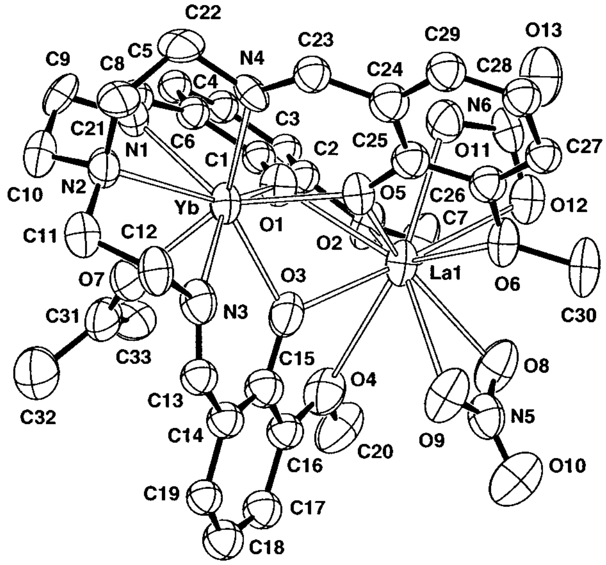

Figure 2. Molecular plot for $\{[LYb(C_3H_6O)La(NO_3)_2]_2La(NO_3)_5(H_2O)\}$, with ellipsoids drawn at the 50% probability level. Selected distances and bond lengths (Å): Yb···La(1) = 3.6337(6), Yb···La(2) = 8.3718(3), Yb−N(1) = 2.494(4), Yb−N(2) = 2.626(4), Yb−N(3) = 2.448(5), Yb−N(4) = 2.466(4), Yb−O(1) = 2.259(3), Yb−O(3) = 2.287(4), Yb−O(5) = 2.329(3), Yb−O(7) = 2.368(3), La(1)−O(1) = 2.539(4), La(1)−O(2) = 2.563(4), La(1)−O(3) = 2.439(4), La(1)−O(4) = 2.797(4), La(1)−O(5) = 2.483(3), La(1)−O(6) = 2.565(4), La(1)−O(8) = 2.616(4), La(1)−O(9) = 2.632(4), La(1)−O(11) = 2.581(4), La(1)−O(12) = 2.661(4). Selected angles (deg): Yb−O(1)−La(1) = 98.3(1), Yb−O(3)−La(1) = 100.5(1), Yb−O(5)−La(1) = 98.0(1). Shortest intermolecular metal−metal distances (Å): Yb···La(1) = 7.8642(6), La(1)···La(1) = 8.828(1), La(1)···La(2) = 8.5375(6), Yb···Yb = 8.3295(1).

The composition of **1′** hypothesized to be $[LYbLa(NO_3)_2]_2[La(NO_3)_5(H_2O)]$ was definitively supported by a structural determination (cf. Table 1), which revealed the presence of discrete cationic and anionic entities. The cationic entity is represented in Figure 2, while a view of the whole $[LYb(C_3H_6O)La(NO_3)_2]_2[La(NO_3)_5(H_2O)]$ entity is given as Supporting Information. The most interesting feature of the cationic unit is the presence of the two metal ions Yb^{3+} and La^{3+} encapsulated by the ligand. These ions are triply bridged one to the other via the three phenolate oxygens from L. The YbO_3La core is asymmetric with Yb−O(*i*) and La−O(*i*) distances (*i* = 1, 3, 5) ranging from 2.259(3) to 2.329(3) Å and from 2.439(4) to 2.539(4) Å, respectively. The variations of the Yb−O(*i*)−La angles are less important, with values of 98.3(1)° (*i* = 1), 100.5(1)° (*i* = 3), and 98.0(1)° (*i* = 5). The resulting Yb···La separation of 3.6337(6) Å is rather short with respect to the mean value (ca. 4.08 Å) of the La···La distance in complexes with a LaO_2La core,[7,23−25] even after correction for the ionic radius difference.[26] Similarly, the La−O(*i*)−Yb angles are smaller than the related La−O−La angles (ca. 110°).[7,23−25]

The ytterbium ion is eight-coordinate, bonding to the three bridging oxygen and the four nitrogen atoms of L, the coordination sphere being completed by an oxygen from a solvent acetone molecule. It may be noted that the tertiary nitrogen N(2), which caps the structure, is "tucked in" with its lone pair of electrons directed at the Yb^{3+} ion. The same

---

(22) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5.

(23) Matthews, K. D.; Kahwa, I. A.; Williams, D. J. *Inorg. Chem.* **1994**, *33*, 1382.

(24) Wang, Z.; Reibenspies, J.; Martell, A. E. *Inorg. Chem.* **1997**, *36*, 629.

(25) Yang, L. N.; Liu, S.; Wang, E.; Rettig, S. J.; Orvig, J. C. *Inorg. Chem.* **1995**, *34*, 2164.

(26) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

disposition has been observed in a mononuclear (Gd or Yb) complex of a tripod ligand.[10] However in the present case, the bonding interaction is weak, as indicated by the N(2)−Y(b) separation of 2.626(4) Å, which is significantly larger than the related distances with imino nitrogens. These N(*j*)−Yb (*j* = 1, 3, 4) distances vary from 2.448(5) to 2.494(4) Å and compare well with the values reported in the literature for mononuclear complexes.[10,25] The two lanthanum ions, La(1) and La(2), are ten-coordinate. In the cationic unit, La(1) is bonded to the three bridging oxygens, the three methoxy oxygens of the side arms, and four oxygens from two bidentate nitrato ions. In the anionic unit, the ten coordination sites of La(2) are filled by ten oxygen atoms from five bidentate NO_3^- ions. One nitrate is disordered in the ratio 50/50. This disorder may be due to the presence of a water molecule hydrogen-bonded to the two alternative positions of the terminal disordered nitrato oxygen. Finally, it may be noted that the cationic and anionic units are well insulated one from the others. The separations between metal ions belonging to neighboring units (from 7.8642(6) to 8.828(1) Å for the shortest ones) are much larger than the Yb−La(1) distance within the cationic unit.

As for the ability of the ligand LH_3 to support magnetic interaction, we have to consider complex **2**, since complexes **1** and **1′** are of little interest because of the diamagnetism of La^{3+} ($^1S_0$ free-ion ground state). The thermal variation of the magnetic susceptibility of **2** is represented in Figure 3 in the form $\chi_M T$ vs T. At 300 K, $\chi_M T$ is equal to 15.7 cm^3 K mol^{-1}, as expected for two isolated Gd^{3+} ions ($^8S_{7/2}$). However, the whole profile of the $\chi_M T$ vs T curve is indicative of an antiferromagnetic behavior, leading to a nonmagnetic ground state for the (Gd, Gd) pair. A quantitative analysis of the data, based on a spin-only Hamiltonian, $H = -J \cdot S_{Gd} S_{Gd'}$, yields $J = -0.104$ cm^{-1} and $g = 1.999$. The J value is perfectly consistent with those recently obtained[8] for complexes with a GdO_2Gd core ($J = -0.140$ and -0.100 cm^{-1} and $g = 2.025$ and 1.976, respectively). Less effective interactions ($J = -0.053$ and -0.045 cm^{-1} and $g = 2.0$, respectively) have also been reported.[6,16]

Regarding the (Yb, La) pair, we note that complexes **1** and **1′** display identical magnetic behaviors. At 300 K, $\chi_M T$ is equal to 2.43 cm^3 K mol^{-1}, which corresponds to a moment of 4.4 μ_B, moments ranging from 4.0 to 4.9 μ_B in the literature[27] for mononuclear ytterbium compounds at room temperature. As T is lowered, $\chi_M T$ decreases more and more rapidly to reach a value of 1.10 cm^3 K mol^{-1} at 4 K. This behavior has to be related to the splitting of the $^2F_{7/2}$ ground state into four Kramers doublets by the crystal field and progressive depopulation of the doublets of higher energy.

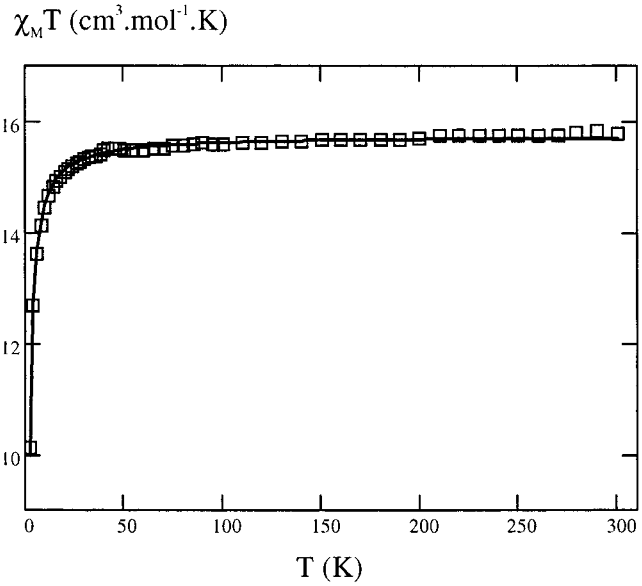

Figure 3. Thermal dependence of $\chi_M T$ for $LGd_2(NO_3)_3 \cdot 3H_2O$ (**2**) at 0.1 T. The full line corresponds to the best data fit.

In our opinion, the main goal of this paper is to afford the first example of a structurally characterized complex involving two different lanthanide ions. The synthetic approach relies on a tripodal ligand with imine linkers. It displays ten potential coordination sites which are all used to encapsulate two identical or different 4f ions. In addition, the magnetic behavior of the homodinuclear (Gd, Gd) complex points out the capability of the ligand to support a significant magnetic interaction between the two f ions. Preliminary data show that the synthetic procedure is not restricted to the (Yb, La) and (Gd, Gd) couples. Further studies of other heterodimetallic complexes are now in progress.

Acknowledgment. We thank Anthony Fonseca for his contribution to the synthetic work, Dr. A. Mari for his aid with the magnetic measurements, and Mrs. S. Richelme (Service Commun de Spectroscopie de Masse) for her help with the mass spectral measurements.

Supporting Information Available: Listings of experimental crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and equations for the least-squares planes and deviations therefrom for $\{[LYb(C_3H_6O)La(NO_3)_2]_2La(NO_3)_5(H_2O)\}$ and a view of the $[LYbLa(NO_3)_2]_2[La(NO_3)_5(H_2O)]$ entity (15 pages). See any current masthead page for ordering instructions.

IC9712481

---

(27) Boudreaux, E. A.; Mulay, L. N. *Theory and Applications of Molecular Paramagnetism*; John Wiley: New York, 1976.